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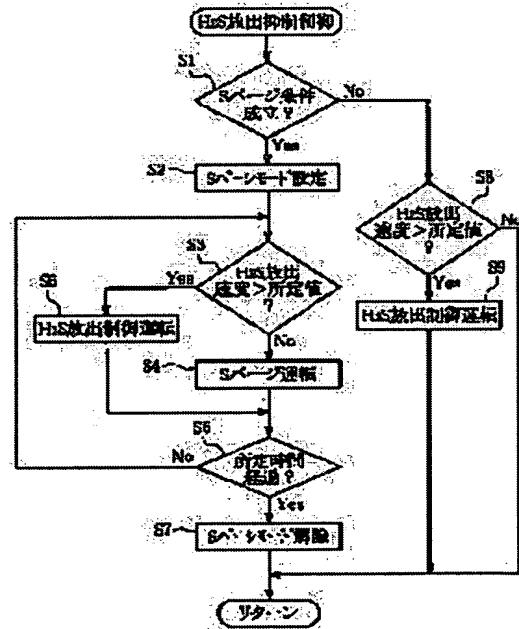
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(54) EXHAUST EMISSION CONTROL DEVICE FOR INTERNAL COMBUSTION ENGINE

(57) Abstract:

PROBLEM TO BE SOLVED: To reproduce the controllability of NOx storage catalyst while restraining the generation of the smell by the discharge of the exhaust gas containing hydrogen sulfide(H2S) to the atmosphere.

SOLUTION: An electronic control unit modulates the target air fuel ratio so that the target air fuel ratio takes a rich side value and lean side value alternately, when a H2S discharge speed estimated based on an engine operation state exceeds a judge value (S6, S9). Consequently, the exhaust air fuel ratio is modulated to the rich side and lean side by nearly making the theoretical air fuel ratio to a standard. When the exhaust air fuel ratio is the rich side the sulfur amount adhered to NOx storage catalyst is removed and the controllability of NOx storage catalyst is reproduced and when the exhaust air fuel ratio is the lean side, the generation of H2S from the sulfur amount discharged from NOx storage catalyst as well as the generation of the smell are restrained.



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CLAIMS

[Claim(s)]

[Claim 1] The NOx occlusion catalyst equipment which emits NOx which carried out occlusion while it was prepared in an internal combustion engine's flueway, and carrying out occlusion of NOx in exhaust gas, when an exhaust air air-fuel ratio was the Lean air-fuel ratio when an exhaust air air-fuel ratio is theoretical air fuel ratio or a rich air-fuel ratio, An air-fuel ratio fluctuation means to fluctuate an exhaust air air-fuel ratio to the rich and Lean side on the basis of theoretical air fuel ratio mostly, The exhaust emission control device of the internal combustion engine characterized by having the control means which operates the above-mentioned air-fuel ratio fluctuation means based on the emission rate of the hydrogen sulfide from the above-mentioned NOx occlusion catalyst equipment presumed based on the above-mentioned internal combustion engine's operational status.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates NOx catalyst equipment to a refreshable exhaust emission control device about an internal combustion engine's exhaust emission control device, controlling the odor by the hydrogen sulfide in exhaust gas (H₂S).

[0002]

[A related background technique] The occlusion mold NOx catalyst is put in practical use in order to purify NOx in a lean combustion internal combustion engine's exhaust gas, but with this kind of catalyst, since occlusion also of the sulfur component in exhaust gas (S component) is carried out on a catalyst in case occlusion of NOx in exhaust gas is temporarily carried out on a catalyst at the time of Lean operation of an internal combustion engine, the problem (S poisoning) that the NOx purification engine performance of a catalyst falls arises.

[0003] Then, while raising the temperature of the occlusion mold NOx catalyst carried out S poisoning, S component in which occlusion was carried out to the catalyst by Lycium chinense into reducing atmosphere in the catalyst is made to secede from a catalyst, and recovering the purification effectiveness is known. However, according to such technique, when S component is made to emit from an occlusion mold NOx catalyst, H₂S are generated, and the new problem that an odor occurs arises.

[0004] With the technique given in JP,8-294618,A, in order to solve this problem, while arranging a downstream catalytic converter on the lower stream of a river of an occlusion mold NOx catalyst, the air-fuel ratio perturbation which fluctuates an air-fuel ratio by turns in a rich region and the Lean region on the basis of theoretical air fuel ratio was performed, the downstream catalytic converter performed capture and oxidation of H₂S, and emission to the atmospheric air of H₂S is controlled.

[0005]

[Problem(s) to be Solved by the Invention] However, when the H₂S emission rate at the time of H₂S being emitted from an occlusion mold NOx catalyst changes with the amounts of occlusion and engine operational status of S component of an NOx catalyst a lot, therefore an air-fuel ratio perturbation is performed regardless of engine operational status, the capture and oxidation of H₂S by the downstream catalytic converter are not fully performed, but it has a possibility that a lot of H₂S may be emitted into atmospheric air, and an odor may occur.

[0006] It aims at offering the exhaust emission control device which can reproduce NOx occlusion catalyst equipment from S poisoning, this invention controlling certainly emission into the atmospheric air of a hydrogen sulfide (H₂S), and preventing generating of an odor.

[0007]

[Means for Solving the Problem] Based on the hydrogen-sulfide emission rate from the NOx occlusion catalyst equipment presumed based on engine operational status, an air-fuel ratio fluctuation means operates under control of a control means, and the exhaust emission control device concerning invention according to claim 1 is characterized by fluctuating an exhaust air air-fuel ratio to the rich and Lean side on the basis of theoretical air fuel ratio mostly by this actuation.

[0008] In the exhaust emission control device concerning invention according to claim 1 Although an exhaust air air-fuel ratio is emitted from NOx occlusion catalyst equipment SUTOIKIO or when rich and, as for the sulfur component in the exhaust gas by which occlusion was carried out to NOx

occlusion catalyst equipment with NOx (S component), a hydrogen sulfide (H₂S) is generated from this emission S component when an exhaust air air-fuel ratio is Lean. In case a hydrogen sulfide is generated and emitted, according to the hydrogen-sulfide emission rate presumed based on engine operational status, an air-fuel ratio fluctuation means can operate under control of a control means. And an exhaust air air-fuel ratio is mostly changed by turns to the rich and Lean side on the basis of theoretical air fuel ratio by actuation of an air-fuel ratio fluctuation means.

[0009] During actuation of an air-fuel ratio fluctuation means, if a hydrogen sulfide is emitted and an exhaust air air-fuel ratio becomes Lean while an exhaust air air-fuel ratio is rich, emission of a hydrogen sulfide will no longer be performed. That is, a hydrogen sulfide will be emitted intermittently and the average value of the emission rate decreases considerably compared with the case where continuation emission of a hydrogen sulfide is permitted without fluctuating an exhaust air air-fuel ratio to the rich and Lean side. Here, a hydrogen-sulfide emission rate is closely connected with the hydrogen-sulfide concentration in exhaust gas, and hydrogen-sulfide concentration is closely connected with the degree of the odor accompanying discharge of a hydrogen sulfide. Thus, the problem of generating of the odor accompanying [can control a hydrogen-sulfide emission rate by fluctuating an exhaust air air-fuel ratio by turns to the rich side and Lean side, when there is a possibility that it may correspond to the degree of an odor while a hydrogen-sulfide emission rate changes with engine operational status, and a hydrogen-sulfide emission rate may increase in this invention, and an odor may become strong, can weaken an odor, and] discharge of a hydrogen sulfide can be eased to dissolution or large width of face. On the other hand, as an average, since an exhaust air air-fuel ratio is held at the value near the theoretical air fuel ratio, it can reproduce the purification capacity of NOx occlusion catalyst equipment. That is, playback of NOx occlusion catalyst equipment will be performed in this invention, an air-fuel ratio fluctuation means operating based on the hydrogen-sulfide emission rate which changes with engine operational status, and preventing generating of the odor by emission of a hydrogen sulfide.

[0010] In invention according to claim 1, preferably, when the hydrogen-sulfide emission rate from NOx catalyst equipment is larger than a predetermined value, an air-fuel ratio fluctuation means is operated. In this case, when a hydrogen-sulfide emission rate exceeds a predetermined value, generating of an odor which exceeds the odor degree corresponding to the predetermined value of a hydrogen-sulfide emission rate is beforehand prevented by operating an air-fuel ratio fluctuation means and reducing a hydrogen-sulfide emission rate.

[0011] The exhaust emission control device concerning invention according to claim 1 is preferably equipped further with an air-fuel ratio fixed means to maintain an exhaust air air-fuel ratio to theoretical air fuel ratio or a rich air-fuel ratio over a predetermined period, and a control means operates an air-fuel ratio fixed means, when the hydrogen-sulfide emission rate from NOx occlusion catalyst equipment is small. In this suitable mode, if an exhaust air air-fuel ratio turns into theoretical air fuel ratio or a rich air-fuel ratio by actuation of an air-fuel ratio fixed means, S component by which occlusion was carried out to NOx occlusion catalyst equipment will be emitted, S poisoning of NOx occlusion catalyst equipment will be mitigated by this, and that purification engine performance will be recovered. Moreover, since the actuation is restricted when a hydrogen-sulfide emission rate is small although a part for S ** as a result and a hydrogen sulfide are emitted by actuation of an air-fuel ratio fixed means, there are few possibilities that an odor may occur during actuation of an air-fuel ratio fixed means. Furthermore, since theoretical-air-fuel-ratio operation or rich air-fuel ratio operation of an internal combustion engine by actuation of an air-fuel ratio fixed means is restricted to a predetermined period, there are few possibilities of causing fuel consumption aggravation.

[0012]

[Embodiment of the Invention] Hereafter, the internal combustion engine equipped with the exhaust emission control device of 1 operation gestalt of this invention is explained. In addition to the fuel injection like an inhalation-of-air line, the internal combustion engine of this operation gestalt consists of injection mold jump-spark-ignition type serial 4-cylinder gasoline engines in a cylinder which can be carried out if needed in the fuel injection like a compression stroke or an expansion line. the fuel-injection mode in this injection mold engine in a cylinder changes to versatility according to change of an engine operation region, the air-fuel ratio of gaseous mixture changes

ranging from the super-RIN air-fuel ratio to a rich air-fuel ratio in connection with this, and improvement in fuel consumption and an exhaust air property is achieved, generating necessary engine power. Although this kind of injection mold engine in a cylinder is conventionally well-known, it explains simple hereafter.

[0013] As shown in drawing 1, the electromagnetic fuel injection valve 6 is attached in the cylinder head 2 of an engine 1 with the ignition plug 4 for every gas column. It connects with a fuel supply system (illustration abbreviation) with a fuel tank, a low voltage fuel pump, and a high-pressure fuel pump through a fuel pipe, and a fuel injection valve 6 can inject the fuel in a fuel tank now directly by desired fuel pressure in a combustion chamber 8 from a fuel injection valve 6.

[0014] A suction port is formed in the abbreviation erection direction for every gas column at the cylinder head 2, and each suction port is open for free passage at the end of an inlet manifold 10. Throttle sensor 11a which detects throttle opening theta_t is prepared in the throttle valve 11 prepared in the other end side of an inlet manifold 10. Moreover, an exhaust air port is formed in an abbreviation horizontal direction for every gas column at the cylinder head 2, and each exhaust air port is open for free passage at the end of an exhaust manifold 12.

[0015] The elevated-temperature sensor 16 which a muffler (not shown) is connected to an exhaust manifold 12 through an exhaust pipe (flueway) 14, and detects an exhaust-gas temperature to an exhaust pipe 14 is formed. The exhaust emission control device of this operation gestalt has the small contiguity three way component catalyst 20 which approached the engine 1 and was allotted in the exhaust pipe 14, and exhaust air purification catalyst equipment 30 arranged in the exhaust pipe 14 on the lower stream of a river of the contiguity three way component catalyst 20. Exhaust air purification catalyst equipment 30 has occlusion mold NOx catalyst (NOx occlusion catalyst equipment) 30a and three way component catalyst (H2S release-inhibiting catalyst equipment) 30b allotted to the lower stream of a river. A reference mark 32 expresses the NOx sensor 32 which is arranged on the lower stream of a river of three way component catalyst 30b, and detects NOx concentration.

[0016] The catalyst kind and barium (Ba) with which occlusion mold NOx catalyst 30a consists of noble metals, such as platinum (Pt) and a rhodium (Rh), The function which once sets NOx to nitrate X-NO₃, and carries out occlusion in an oxidizing atmosphere including the NOx occlusion agent which consists of alkali metal and alkaline earth metal, such as a potassium (K), It has the function to which N₂ (nitrogen) etc. is made to return NOx into the reducing atmosphere in which CO mainly exists. Occlusion of the oxide SO_x of not only NOx but the sulfur component contained in exhaust gas is carried out to this occlusion mold NOx catalyst 30a as sulfate X-SO₄, such as a barium sulfate BaSO₄. As shown in the following reaction formula, this sulfate X-SO₄ turns into SO₂, when occlusion mold NOx catalyst 30a is exposed to reducing atmosphere, and a hydrogen sulfide (H₂S) is generated in this case.

[0017] Although the so-called compulsive S purge which makes gaseous mixture rich is periodically carried out while planning removal of a sulfate and raising whenever [NOx catalyst temperature] generally since that NOx purification effectiveness will fall if the sulfate has adhered to BaSO₄+CO->BaCO₃+SO₂SO₂+H₂->H₂S+O₂NOx catalyst 30a, H₂S which release a nasty smell in this case are generated. Moreover, since whenever [NOx catalyst temperature] goes up while an engine 1 is operated with a rich air-fuel ratio when an engine 1 is operated like [at the time of climb way transit of a car, and acceleration operation] in a heavy load region, from a sulfate, SO₂ ****s, and is emitted and H₂S are generated in connection with this (nature S purge).

[0018] The amount of generation of H₂S becomes so large that the coating weight of the sulfate (S component) to NOx catalyst 30a increases so that clearly from the above-mentioned reaction formula. There is it compared with the case of a three way component catalyst, many the coating weight of occlusion, i.e., amount, of S component to an NOx catalyst, and it has the inclination for a lot of H₂S to be generated, in the exhaust emission control device equipped with the NOx catalyst. With this operation gestalt, the nickel oxide as an H₂S release-inhibiting agent is added to three way component catalyst 30b in order to control emission of H₂S to the atmospheric air under compulsive S purge and nature S purge. Three way component catalyst 30b which this nickel oxide acts so that H₂S emitted from NOx catalyst 30a may be made to convert into a nickel sulfide as shown in the following reaction formula, therefore comes to add nickel oxide will do so the function which carries

out occlusion of H₂S. H₂S by which **** occlusion was carried out react with oxygen in an oxidizing atmosphere, and are converted and emitted to SO₂ with few odors.

[0019] Although the H₂S occlusion capacity of three way component catalyst 30b increases so that from the reaction formula of the H₂ S+NiO->NiS+O₂NiS+3/2*O₂ ->NiO+SO₂ above, and there are many additions of the nickel oxide to three way component catalyst 30b, on the other hand, there is an inclination for the 3 yuan function of three way component catalyst 30b to fall.

[0020] With this operation gestalt, 10g or more per capacity of 11. of three way component catalyst 30b of lower limits of the addition of nickel oxide is preferably set to the value of 15g or more in order to collateralize H₂S occlusion capacity which makes occlusion of H₂S possible, also when H₂S are emitted so much from NO_x catalyst 30a. Moreover, 35g or less of upper limits of the addition of nickel oxide is preferably set to the value of 25g or less in order to stop to what can permit the fall of the 3 yuan function of three way component catalyst 30b. In addition, it can replace with nickel oxide, nickel may be added, and the bound value of the addition of nickel can be calculated by converting into the bound value of a nickel oxide addition in this case. Furthermore, Pd, Mn, Fe, Zn, Co, Cu, etc. may be used as an H₂S release-inhibiting agent. Although the addition of an H₂S release-inhibiting agent differs in the suitable value since H₂S release inhibiting changes with classes of additive, the value of 30% thru/or 300% of within the limits is suitable for it at the mole ratio to an NO_x occlusion agent addition.

[0021] According to the exhaust emission control device of this operation gestalt constituted as mentioned above, also in the time of the cold starting of an engine 1 etc., the contiguity three way component catalyst 20 is activated promptly, and exhaust air purification is performed, and occlusion of NO_x is carried out by NO_x catalyst 30a at the time of the Lean combustion operation of an engine 1. Furthermore, at the time of the nature S purge accompanying the engine operation in a heavy load region, occlusion of the H₂S emitted from NO_x catalyst 30a is carried out by three way component catalyst 30b of NiO addition in the form of NiS, and discharge of H₂S into atmospheric air is controlled.

[0022] Operation of compulsive S purge (sulfur component emission control to which emission of S component from an NO_x catalyst is generally urged) of it is attained so that the exhaust emission control device of this operation gestalt may maintain the necessary NO_x purification effectiveness of NO_x catalyst 30a. This compulsive S purge is carried out under control of the control means of an exhaust emission control device. With this operation gestalt, the electronic control unit (ECU) 40 which manages the operation control of an engine 1 has the function of this control means simultaneously.

[0023] ECU40 is equipped with an I/O device, storage (ROM, RAM, nonvolatile RAM, etc.), a central processing unit (CPU), a timer counter, etc., the various sensors of throttle sensor 11a, the crank angle sensor 13, the elevated-temperature sensor 16, and NO_x sensor 32 grade are connected to the input side, and the ignition plug 4 and the fuel injection valve 6 grade are connected to the output side.

[0024] In relation to engine operation control, ECU40 calculates fuel oil consumption, ignition timing, etc. while choosing fuel-injection mode based on the detection information inputted from various sensors. For example, based on throttle opening information theta from throttle sensor 11a, and the engine-speed information Ne detected based on the crank angle information from the crank angle sensor 13, the target cylinder internal pressure (target mean effective pressure Pe) corresponding to an engine load is called for, and fuel-injection mode is set up according to this target mean effective pressure Pe and the engine-speed information Ne. And fuel oil consumption is determined based on the target air-fuel ratio (target A/F) set up from the target mean effective pressure Pe and an engine speed Ne.

[0025] With this operation gestalt, the H₂S release-inhibiting control routine shown in drawing 2 is carried out by ECU40, and is made to perform compulsive S purge by this control routine. In addition, although Air Fuel Ratio Control for an NO_x purge is carried out under control of ECU40, this Air Fuel Ratio Control is conventionally well-known, and omits the explanation. It is distinguished in the H₂S release-inhibiting control routine of drawing 2 whether S purge conditions are satisfied (step S1). various S purge conditions can distinguish formation of S purge conditions, when the sum total execution time of the Lean combustion operation from the time of it being alike

and the last compulsive S purge being completed that it can set up reaches predetermined time. When the estimate Qs of SOx by which occlusion was carried out to NOx catalyst 30a reaches the specified quantity, he is trying to distinguish formation of S purge conditions with this operation gestalt.

[0026] The amount Qs of presumed SOx occlusion is calculated for example, from a degree type (1) in this S purge condition distinction.

$Qs = Qs(n-1) + \Delta Qf \cdot K \cdot Rs$ -- (1)
K=K1, K2, K3 -- (2)
 $Rs = \alpha \cdot R_1, R_2, dT$ -- (3)

Here, as for $Qs(n-1)$, the last value of the amount of presumed SOx occlusion and ΔQf show the amount of fuel-injection addition per execution cycle of this control routine.

[0027] K is a correction factor calculated from the above-mentioned formula (2), and is expressed with the product of three S poisoning multipliers K1, K2, and K3 which expresses the poisoning degree according to each of Tcat whenever [S content / in air-fuel ratio A/F and a fuel /, and catalyst temperature]. Rs shows the amount of emission S per control-routine execution cycle, and is calculated from the above-mentioned formula (3). α is a rate of emission per unit time amount (set point) among a formula (3), dT shows the execution cycle of a fuel-injection control routine, and R_1 and R_2 show the emission capacity multiplier according to each of Tcat and air-fuel ratio A/F whenever [catalyst temperature].

[0028] Tcat is calculated whenever [catalyst temperature] by amending the exhaust-gas temperature detected by the elevated-temperature sensor 16 using the correction factor and the exhaust air rate of flow which were read from the temperature compensation map (illustration abbreviation). A temperature compensation map is beforehand set up by experiment etc., and amendment with Tcat and an exhaust-gas temperature is given in this temperature compensation map with the function of the target mean effective pressure Pe and the engine-speed information Ne whenever [catalyst temperature / at the time of a stationary].

[0029] When formation of S purge conditions is distinguished at step S1, it is started after the timer which measures the elapsed time from S purge mode setting point in time is reset, while S purge mode is set up (step S2). And it is distinguished whether the increment degree of an H2S emission rate, i.e., H2S concentration to time amount, has exceeded the predetermined value (step S3).

[0030] Although an H2S emission rate may be detected from the actual H2S emission rate information detected by the sensor, he is trying for engine-speed Ne, the target mean effective pressure Pe, and 1 inhalation-of-air line to presume an H2S emission rate with this operation gestalt based on the engine operation condition expressed with functions, such as Tcat, an exhaust-gas temperature, and engine-coolant water temperature, whenever [neighboring inhalation air content A/N, vehicle speed, and catalyst temperature].

[0031] That is, the experiment which finds the H2S emission rate in various engine operation conditions is conducted, and based on an experimental result, a map is created beforehand and stored in the storage of ECU40. And the H2S emission rate according to an engine operation condition will be found from this map during the engine operation under control of ECU40. Although illustration is omitted, generally in a map, an engine operation condition and an H2S emission rate are associated so that an H2S emission rate may increase along with the rise of Tcat or an exhaust-gas temperature whenever [increase and catalyst temperature]. [of an engine speed Ne or an engine load (the target mean effective pressure Pe, inhalation air content A/N)]

[0032] The predetermined value for the judgment of an H2S emission rate is set as the value (henceforth threshold value) corresponding to the lower limit of H2S concentration for which people who are near the outlet of an exhaust pipe 14 are made to sense the odor of H2S. This threshold value changes especially according to the vehicle speed. That is, even if H2S are emitted from an exhaust pipe 14 at the time of car transit, H2S will be promptly diffused into atmospheric air, and the threshold value which senses an odor becomes comparatively high. On the other hand, at the time of a car transit halt, it is hard to diffuse H2S, and threshold value becomes a small thing. Therefore, it is desirable to set up the predetermined value of an H2S emission rate according to the vehicle speed, and with this operation gestalt, he map-izes beforehand threshold value expressed as a function of the vehicle speed, and is trying to read the threshold value which becomes settled according to the vehicle speed from a map (illustration abbreviation). However, carrying out an adjustable setup of the predetermined value of an H2S emission rate may use a fixed value rather than it is

indispensable.

[0033] Generally, if it is immediately after S purge mode setting, an H₂S emission rate does not exceed a predetermined value, but the distinction result in step S3 is denied (No). Thus, when the requirements that an H₂S emission rate is small are satisfied, S purging operation is performed (step S4). In S purging operation, target A/F is set as a predetermined rich air-fuel ratio (for example, 12), and rich air-fuel ratio operation is carried out in order to expose occlusion mold NO_x catalyst 30a to reducing atmosphere, and let an exhaust air air-fuel ratio be a rich air-fuel ratio. Moreover, the lag of the ignition timing is carried out, exhaust gas temperature is raised and, thereby, the temperature up of the NO_x catalyst 30a is carried out. By the engine operation in such a rich air-fuel ratio, the incomplete combustion of a fuel happens, the carbon monoxide and hydrocarbon of a sulfur oxide SO_x required for removal are generated so much, NO_x catalyst 30a is supplied, and S purge is conjointly promoted with the rise of whenever [accompanying the exhaust air temperature rise by lag control of ignition timing / NO_x catalyst temperature].

[0034] With this operation gestalt, fuel oil consumption is determined by ECU40 based on target A/F set up as mentioned above, and the closing motion drive of the fuel injection valve 6 is carried out according to the driving signal corresponding to this fuel oil consumption, and an inhalation air content is adjusted if needed. Therefore, an air-fuel ratio fixed means to maintain an exhaust air air-fuel ratio to theoretical air fuel ratio or a rich air-fuel ratio over a predetermined period with the timer of built-in in the control bulb element (illustration abbreviation) and ECU40 concerning ECU40, a fuel injection valve 6, and inhalation air content adjustment will be constituted.

[0035] Now, although H₂S will be generated under a rich air-fuel ratio if emission of SO_x progresses by advance of S purge, H₂S are converted into a nickel sulfide with the nickel oxide added by three way component catalyst 30b prepared in the lower stream of a river of NO_x catalyst 30a. Thus, since occlusion of H₂S is carried out to three way component catalyst 30b, H₂S concentration in the exhaust gas emitted into atmospheric air is reduced.

[0036] With reference to the time amount with the passage of time by the timer started at step S2, it is judged following step S4 concerning S purging operation whether S purge mode was maintained over predetermined time (predetermined period) (step S5). If S purge maintenance time amount does not fulfill predetermined time, it judges that S component removal from NO_x catalyst 30b is not fully performed, and returns to step S3. In addition, the judgment of termination of S purging operation may judge as conditions that the amount Q_s of presumed SO_x occlusion becomes below the specified quantity.

[0037] Although occlusion of the H₂S generated with reduction of S component in NO_x catalyst 30a as mentioned above is carried out to three way component catalyst 30b, an H₂S emission rate may increase temporarily during S purging operation by the reasons of there being many amounts of S components by which occlusion was carried out to NO_x catalyst 30a. In this case, the change to H₂S release-inhibiting operation from S purging operation is performed so that it may reduce an H₂S emission rate, if it is distinguished at step S3 that the H₂S emission rate exceeded the predetermined rate (step S6).

[0038] In this H₂S release-inhibiting operation, target A/F is modulated by ECU40 bordering on theoretical air fuel ratio. Namely, as shown in drawing 3 , target A/F is set as 1st target A/F by the side of rich, or 2nd target A/F by the side of Lean by turns for every predetermined period Tcycle. Here, 1st and 2nd target A/F is set as a value which makes S purge a promotion possible value (for example, SURAITO rich about 14.3 or about 12 by the side of rich), respectively in the average value of target A/F under H₂S release-inhibiting operation. And fuel oil consumption is determined by ECU40 based on target A/F set up by carrying out in this way, and the closing motion drive of the fuel injection valve 6 is carried out according to this fuel-oil-consumption data, and an inhalation air content is adjusted if needed. Therefore, ECU40 constitutes an air-fuel ratio fluctuation means to fluctuate an exhaust air air-fuel ratio by turns to the rich and Lean side on the basis of theoretical air fuel ratio mostly with the control bulb element (illustration abbreviation) concerning a fuel injection valve 6 or inhalation air content adjustment.

[0039] The above-mentioned H₂S release-inhibiting operation plans to utilize for the maximum the H₂S occlusion and the emission function of the nickel oxide added by three way component catalyst 30b. That is, before the H₂S occlusion operation (H₂ S+NiO->NiS+O₂) by the nickel oxide in rich

air-fuel ratio operation (reducing atmosphere) is saturated, H₂S by which occlusion was carried out to a change and three way component catalyst 30b in the form of a nickel sulfide are converted into SO₂ with few odors from rich air-fuel ratio operation to the Lean air-fuel ratio operation (oxidizing atmosphere) (NiS+3 / 2*O₂ ->NiO+SO₂).

[0040] In addition, it replaces with the above-mentioned A/F modulation which changes an air-fuel ratio a predetermined period between a rich air-fuel ratio and the Lean air-fuel ratio, and may be made to carry out rich air-fuel ratio operation covering predetermined rich-ized time amount, and the Lean air-fuel ratio operation covering the predetermined Lean-ized time amount by turns. In this case, it is desirable that saturation time and the emission time amount which takes S component caught in the form of a nickel sulfide to emit as SO₂ take [S component prehension operation by the nickel oxide added by three way component catalyst 30b comes to be saturated to take into consideration] into consideration to change according to an engine operation condition etc., and sets up rich-ized time amount and the Lean-ized time amount in it. That is, each of rich-ized time amount and the Lean-ized time amount is preferably set as a value equal to the saturation time and emission time amount which are decided according to an engine operation condition etc. However, even if it sets rich-ized time amount and the Lean-ized time amount as a fixed value, H₂S depressor effect can be acquired.

[0041] Drawing 4 shows the case where an A/F modulation from which an average air-fuel ratio serves as a value 14.3 in charge of H₂S concentration in the exhaust gas of the three way component catalyst 30b lower stream of a river accompanying the temperature rise of NO_x catalyst 30a by lag control of ignition timing when an air-fuel ratio is maintained to constant value 14.3 is performed. Although an air-fuel ratio is equivalent by performing the A/F modulation which changes an air-fuel ratio periodically between a rich side and the Lean side during engine operation compared with the case of engine operation with a fixed air-fuel ratio so that drawing 4 may show, it turns out that emission of H₂S is controlled.

[0042] If H₂S release-inhibiting operation at step S6 is carried out, H₂S concentration in exhaust gas will decrease, therefore an H₂S emission rate will also decrease. By the fall of this H₂S emission rate, the degree of the odor accompanying H₂S emission decreases. At step S5 following step S6, it is distinguished from S purge mode setting point in time whether predetermined time passed, and if this distinction result is negation, it will return to step S3.

[0043] Thus, according to whether an H₂S emission rate exceeds a predetermined value, S purging operation or H₂S release-inhibiting operation is alternatively carried out until predetermined time passes since S purge mode setting time. And it is judged that the emission of S component by which occlusion was carried out to NO_x catalyst 30a, i.e., playback of the purification capacity of NO_x catalyst 30a, was fully performed when distinguished at step S5 that predetermined time has passed since S purge mode setting time, S purge mode is canceled (step S7), and compulsive S purge control is completed.

[0044] If the failure of S purge conditions is distinguished in step S1, it will be distinguished whether the H₂S emission rate has exceeded the predetermined value (step S8). Since a judgment at this step S8 is performed like a judgment at the above-mentioned step S3, that explanation is omitted. And if it is distinguished at step S8 that the H₂S emission rate has exceeded the predetermined value, H₂S release-inhibiting operation will be performed (step S9). H₂S release-inhibiting operation by step S9 is the same as that of the thing of the above-mentioned step S6, and omits the explanation. If an H₂S emission rate increases by nature S purge also when it is not during S purging operation as mentioned above for example, H₂S release-inhibiting operation will be carried out, and generating of the odor accompanying emission of H₂S is prevented beforehand.

[0045] This invention is not limited to the thing of the above-mentioned operation gestalt, but is deformable to versatility. For example, although it was made to carry out sulfur component emission control (compulsive S purge) to which emission of the sulfur component from NO_x catalyst 30a is urged with the above-mentioned operation gestalt Since an H₂S emission rate can be controlled by carrying out the A/F modulation (step S9 of drawing 2) of the above-mentioned operation gestalt, for example even if it faces the exhaust emission control device of this invention the emission of H₂S by nature S purge, it is not indispensable to carry out compulsive S purge (air-fuel ratio immobilization) by this invention.

[0046] Moreover, although the three way component catalyst was formed in the lower stream of a river of the NOx catalyst of exhaust air purification catalyst equipment as an H₂S release-inhibiting catalyst while the exhaust air purification catalyst equipment arranged on a contiguity three way component catalyst and its lower stream of a river constituted the catalyst system of an exhaust emission control device from the operation gestalt, in this invention, such a configuration is not indispensable and should just be equipped with the NOx occlusion catalyst equipment which discharges [occlusion and] NOx in exhaust gas. And also in the exhaust emission control device which does not possess an H₂S release-inhibiting catalyst on the lower stream of a river of NOx occlusion catalyst equipment, it is refreshable in the purification capacity of the NOx occlusion catalyst equipment carried out S poisoning, controlling generating of the odor by emission H₂S by carrying out the above-mentioned A/F modulation, corresponding to the H₂S emission rate from NOx occlusion catalyst equipment.

[0047] When performing sulfur component emission control (compulsive purge S) in this invention, although the control means for compulsive purge S can constitute from a temperature-up control means to which the temperature up of the Air Fuel Ratio Control means (air-fuel ratio fixed means) and the NOx occlusion catalyst equipment which controls the air-fuel ratio of the gaseous mixture supplied to an internal combustion engine to a rich air-fuel ratio like an operation gestalt carries out, it is not limited to this but can constitute the compulsive S purge control means which consists of either an Air Fuel Ratio Control means or a temperature-up control means.

[0048] Although a temperature up control means is good also as a configuration which consists of an ignition timing control means to which the lag of the ignition timing is carried out like an operation gestalt, it is not limited to this. For example, in the case of the lean combustion internal combustion engine of the injection type in a cylinder, the fuel-injection control means to which additional fuel injection is made to carry out like an expansion line in addition to main fuel injection can constitute a temperature up control means. Moreover, a temperature up control means may carry out the temperature up of the NOx occlusion catalyst equipment further in assistance, when the temperature of NOx occlusion catalyst equipment becomes more than the temperature suitable for the desorption of the sulfur component by which occlusion was carried out more highly than the activity temperature to NOx occlusion catalyst equipment, or laying temperature lower than it.

[0049] according to the exhaust emission control device equipped with compulsive S purge control means, when the amount of occlusion of the sulfur component (S component) by NOx occlusion catalyst equipment increases, sulfur component emission control (S purge) carries out -- having -- consequently, NOx occlusion catalyst equipment -- a rich air-fuel ratio -- and -- or it is exposed to a hot ambient atmosphere, and is urged to emission of S component from NOx occlusion catalyst equipment, and necessary NOx purification effectiveness is maintained.

[0050] Moreover, when compulsive S purge control means may follow catalyst regeneration information or the poisoning information by the sulfur component, and is based on catalyst regeneration information, for example, it is distinguished that the catalyst regeneration frequency within a predetermined period (frequency where desorption of a sulfur component is performed) is lower than predetermined frequency, or when the amount of poisoning presumed from poisoning information is larger than a predetermined value, it is easy to perform sulfur component emission control. Poisoning information can be searched for from a lean combustion internal combustion engine's fuel consumption and operation time (car mileage), or the output of the NOx sensor which detects the NOx concentration in exhaust gas.

[0051]

[Effect of the Invention] The exhaust emission control device of this invention operates an air-fuel ratio fluctuation means based on the hydrogen-sulfide emission rate from the NOx occlusion catalyst equipment presumed based on engine operational status. The purification capacity of the NOx catalyst equipment carried out S poisoning is reproducible, controlling generating of the odor by emission into the atmospheric air of the exhaust gas containing a hydrogen sulfide (H₂S), since an exhaust air air-fuel ratio is mostly fluctuated to the rich and Lean side on the basis of theoretical air fuel ratio by this.

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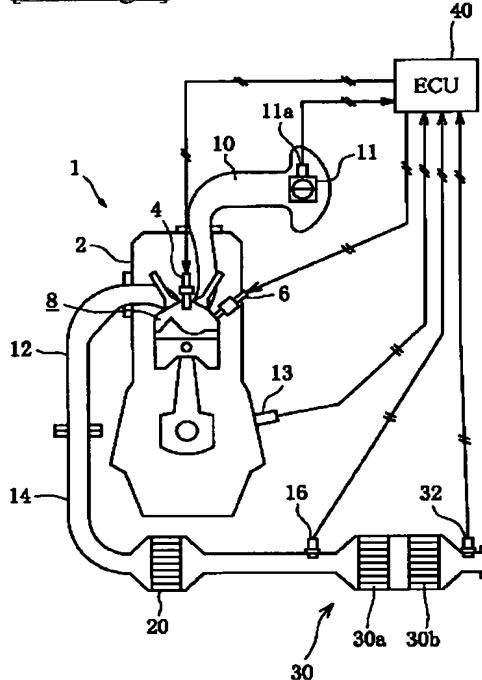
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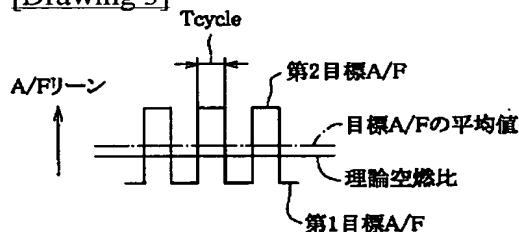
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DRAWINGS

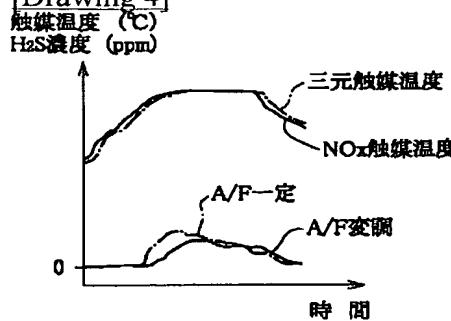
[Drawing 1]



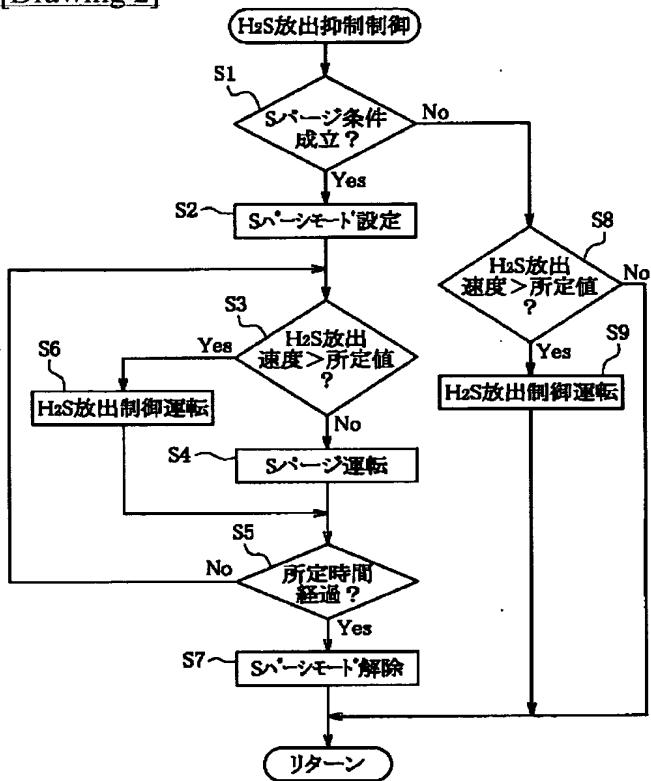
[Drawing 3]



[Drawing 4]



[Drawing 2]



[Translation done.]



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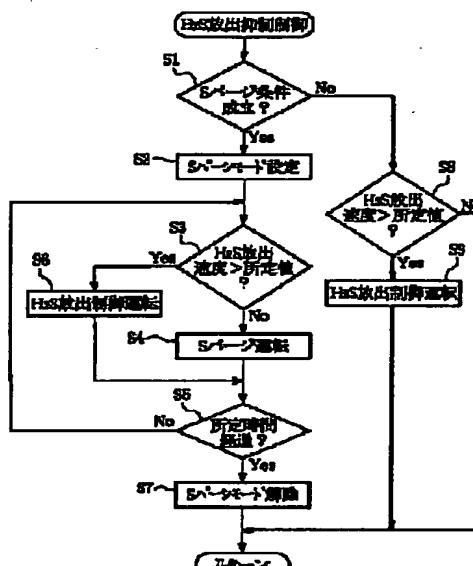
**(54) EXHAUST EMISSION CONTROL DEVICE FOR
INTERNAL COMBUSTION ENGINE**

generation of the smell are restrained.

(57) Abstract

PROBLEM TO BE SOLVED: To reproduce the controllability of NO_x storage catalyst while restraining the generation of the smell by the discharge of the exhaust gas containing hydrogen sulfide(H₂S) to the atmosphere.

SOLUTION: An electronic control unit modulates the target air fuel ratio so that the target air fuel ratio takes a rich side value and lean side value alternately, when a H₂S discharge speed estimated based on an engine operation state exceeds a judge value (S6, S9). Consequently, the exhaust air fuel ratio is modulated to the rich side and lean side by nearly making the theoretical air fuel ratio to a standard. When the exhaust air fuel ratio is the rich side the sulfur amount adhered to NO_x storage catalyst is removed and the controllability of NO_x storage catalyst is reproduced and when the exhaust air fuel ratio is the lean side, the generation of H₂S from the sulfur amount discharged from NO_x storage catalyst as well as the



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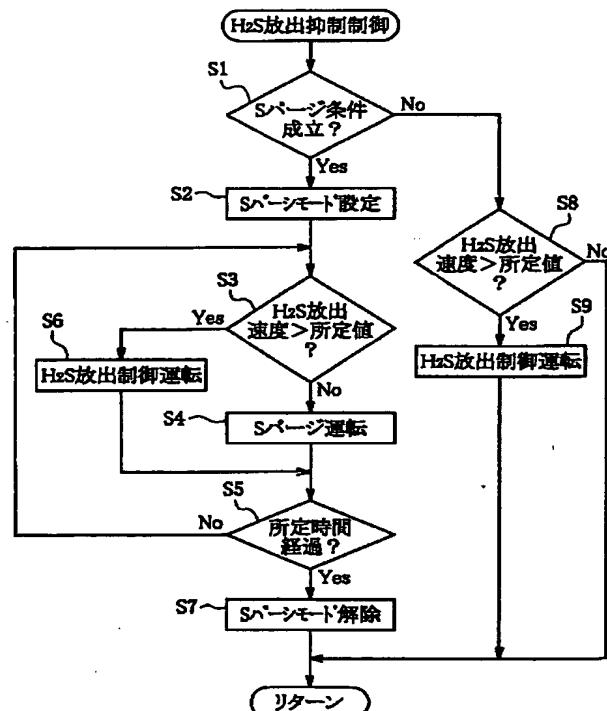
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(54)【発明の名称】 内燃機関の排気浄化装置

(57)【要約】

【課題】 硫化水素(H₂S)を含む排ガスの大気中への放出による臭気の発生を抑制しつつ、NO_x吸蔵触媒の浄化能力を再生する。

【解決手段】 電子制御ユニットは、エンジン運転状態に基づいて推定したH₂S放出速度が判定値を上回ると、目標空燃比がリッチ側の値とリーン側の値を交互にとるよう目標空燃比を変調する(S6、S9)。この結果、排気空燃比は、ほぼ理論空燃比を基準としてリッチ側とリーン側とに変動する。排気空燃比がリッチ側になると、NO_x吸蔵触媒に付着した硫黄分が除去され、NO_x吸蔵触媒の浄化能力の再生が行われ、排気空燃比がリーン側になると、NO_x吸蔵触媒から放出された硫黄分からのH₂Sの生成ひいては臭気の発生が抑制される。



【特許請求の範囲】

【請求項1】 内燃機関の排気通路に設けられ排気空燃比がリーン空燃比のときに排ガス中のNO_xを吸収すると共に吸収したNO_xを排気空燃比が理論空燃比またはリッチ空燃比のときに放出するNO_x吸収触媒装置と、ほぼ理論空燃比を基準に排気空燃比をリッチ側とリーン側とに変動させる空燃比変動手段と、上記内燃機関の運転状態に基づいて推定される上記NO_x吸収触媒装置からの硫化水素の放出速度に基づいて上記空燃比変動手段を作動させる制御手段とを備えることを特徴とする内燃機関の排気浄化装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、内燃機関の排気浄化装置に関し、特に、排ガス中の硫化水素(H₂S)による臭気を抑制しつつNO_x触媒装置を再生可能な排気浄化装置に関する。

【0002】

【関連する背景技術】希薄燃焼内燃機関の排ガス中のNO_xを浄化するべく吸蔵型NO_x触媒が実用化されているが、この種の触媒では、内燃機関のリーン運転時に排ガス中のNO_xを触媒上に一時的に吸蔵する際に排ガス中の硫黄成分(S成分)も触媒上に吸蔵されるため、触媒のNO_x浄化性能が低下するという問題(S被毒)が生じる。

【0003】そこで、S被毒された吸蔵型NO_x触媒の温度を高めると共に触媒を還元雰囲気内におくことにより、触媒に吸蔵されたS成分を触媒から離脱させ、その浄化効率を回復させることができている。しかし、この様な手法によれば、吸蔵型NO_x触媒からS成分を放出させたときにH₂Sが生成され、臭気が発生するという新たな問題が生じる。

【0004】この問題を解消するため、特開平8-294618号公報に記載の技術では、吸蔵型NO_x触媒の下流に下流側触媒コンバータを配置すると共に、理論空燃比を基準としてリッチ域およびリーン域に空燃比を交互に変動させる空燃比バーチャーベーションを行い、下流側触媒コンバータによりH₂Sの捕獲および酸化を行ってH₂Sの大気への放出を抑制している。

【0005】

【発明が解決しようとする課題】しかしながら、吸蔵型NO_x触媒からH₂Sが放出される際のH₂S放出速度は、NO_x触媒のS成分の吸蔵量や機関運転状態によって大きく変化し、従って、機関運転状態に無関係に空燃比バーチャーベーションを実行すると、下流側触媒コンバータによるH₂Sの捕獲及び酸化が充分に行われず、多量のH₂Sが大気中へ放出されて臭気が発生するおそれがある。

【0006】本発明は、硫化水素(H₂S)の大気中への放出を確実に抑制して臭気の発生を防止しつつ、NO

x吸蔵触媒装置をS被毒から再生できる排気浄化装置を提供することを目的とする。

【0007】

【課題を解決するための手段】請求項1に記載の発明に係る排気浄化装置は、機関運転状態に基づいて推定されるNO_x吸蔵触媒装置からの硫化水素放出速度に基づいて制御手段の制御下で空燃比変動手段が作動し、この作動により、ほぼ理論空燃比を基準にして排気空燃比をリッチ側とリーン側とに変動させることを特徴とする。

【0008】請求項1に記載の発明に係る排気浄化装置では、排気空燃比がリーンであるときにNO_x吸蔵触媒装置にNO_xとともに吸蔵された排ガス中の硫黄成分

(S成分)は、排気空燃比がストイキオまたはリッチであるときにNO_x吸蔵触媒装置から放出され、この放出S成分から硫化水素(H₂S)が生成されるが、硫化水素が生成、放出される際、機関運転状態に基づいて推定された硫化水素放出速度に応じて制御手段の制御下で空燃比変動手段が作動可能である。そして、空燃比変動手段の作動により、排気空燃比がほぼ理論空燃比を基準にしてリッチ側とリーン側とに交互に変動する。

【0009】空燃比変動手段の作動中、排気空燃比がリッチである間は硫化水素が放出され、排気空燃比がリーンになると硫化水素の放出は行われなくなる。すなわち、硫化水素は断続的に放出されることになり、その放出速度の平均値は、排気空燃比をリッチ側とリーン側とに変動させずに硫化水素の連続放出を許容する場合に比べ、かなり減少する。ここで、硫化水素放出速度は排ガス中の硫化水素濃度と密接に関連し、また、硫化水素濃度は硫化水素の排出に伴う臭気の度合と密接に関連する。

この様に、硫化水素放出速度は、機関運転状態によって変化すると共に臭気の度合に対応するものであり、本発明では、硫化水素放出速度が増大して臭気が強まるおそれがある場合に排気空燃比をリッチ側とリーン側とに交互に変動させることにより硫化水素放出速度を抑制して臭気を弱めることができ、硫化水素の排出に伴う臭気の発生という問題を解消または大幅に緩和できる。その一方で、排気空燃比が、平均として、理論空燃比近傍の値に保持されるので、NO_x吸蔵触媒装置の浄化能力を再生することができる。すなわち、本発明では、機関運転状態によって変化する硫化水素放出速度に基づいて空燃比変動手段が作動し、硫化水素の放出による臭気の発生を防止しつつ、NO_x吸蔵触媒装置の再生が行われることになる。

【0010】請求項1に記載の発明において、好ましくは、NO_x触媒装置からの硫化水素放出速度が所定値より大きいときに空燃比変動手段を作動させる。この場合、硫化水素放出速度が所定値を上回ったときに空燃比変動手段を作動させて硫化水素放出速度を低下させることにより、硫化水素放出速度の所定値に対応する臭気度合を上回るような臭気の発生が未然に防止される。

【0011】請求項1に記載の発明に係る排気浄化装置は、好ましくは、排気空燃比を所定期間にわたり理論空燃比またはリッチ空燃比に維持する空燃比固定手段を更に備え、制御手段は、NOx吸蔵触媒装置からの硫化水素放出速度が小さいときに空燃比固定手段を作動させる。この好適態様では、空燃比固定手段の作動により排気空燃比が理論空燃比またはリッチ空燃比になると、NOx吸蔵触媒装置に吸蔵されていたS成分が放出され、これによりNOx吸蔵触媒装置のS被毒が軽減されてその浄化性能が回復する。また、空燃比固定手段の作動によりS成分ひいては硫化水素が放出されるものの、その作動は硫化水素放出速度が小さいときに限られるので、空燃比固定手段の作動中に臭気が発生するおそれは少ない。更に、空燃比固定手段の作動による内燃機関の理論空燃比運転またはリッチ空燃比運転が所定期間に限られるので、燃費悪化を来すおそれが少ない。

【0012】

【発明の実施の形態】以下、本発明の一実施形態の排気浄化装置を装備した内燃機関を説明する。本実施形態の内燃機関は、吸気行程での燃料噴射に加えて、圧縮行程や膨張行程での燃料噴射を必要に応じて実施可能な筒内噴射型火花点火式直列4気筒ガソリンエンジンから構成されている。この筒内噴射型エンジンでの燃料噴射モードは、エンジン運転域の変化に応じて種々に変化し、これに伴って混合気の空燃比が超リーン空燃比からリッチ空燃比にわたって変化し、所要のエンジン出力を発生しつつ燃費及び排気特性の向上が図られる。この種の筒内噴射型エンジンは従来公知であるが、以下、簡略に説明する。

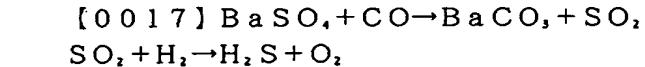
【0013】図1に示すように、エンジン1のシリンダヘッド2には各気筒毎に点火プラグ4とともに電磁式の燃料噴射弁6が取り付けられている。燃料噴射弁6は、燃料タンク、低圧燃料ポンプおよび高圧燃料ポンプを有した燃料供給装置(図示略)に燃料パイプを介して接続され、燃料タンク内の燃料を燃料噴射弁6から燃焼室8内に所望の燃圧で直接に噴射できるようになっている。

【0014】シリンダヘッド2には各気筒毎に略直立方向に吸気ポートが形成され、各吸気ポートは吸気マニホールド10の一端に連通している。吸気マニホールド10の他端側に設けられたスロットル弁11には、スロットル開度θ_{th}を検出するスロットルセンサ11aが設けられている。また、シリンダヘッド2には各気筒毎に略水平方向に排気ポートが形成され、各排気ポートは排気マニホールド12の一端に連通している。

【0015】排気マニホールド12には排気管(排気通路)14を介してマフラー(図示せず)が接続され、また、排気管14には排気温度を検出する高温センサ16が設けられている。本実施形態の排気浄化装置は、エンジン1に近接して排気管14内に配された小型の近接三元触媒20と、排気管14内において近接三元触媒20

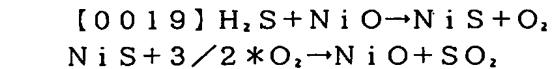
の下流に配された排気浄化触媒装置30とを有している。排気浄化触媒装置30は、吸蔵型NOx触媒(NOx吸蔵触媒装置)30aと、その下流に配された三元触媒(H₂S放出抑制触媒装置)30bとを有している。参照符号32は、三元触媒30bの下流に配されNOx濃度を検出するNOxセンサ32を表す。

【0016】吸蔵型NOx触媒30aは、白金(Pt)、ロジウム(Rh)等の貴金属からなる触媒種とバリウム(Ba)、カリウム(K)等のアルカリ金属やアルカリ土類金属からなるNOx吸蔵剤とを含むものであって、酸化雰囲気においてNOxを一旦硝酸塩X-NO_xとして吸蔵する機能と、主としてCOの存在する還元雰囲気においてNOxをN₂(窒素)等に還元させる機能を持つ。この吸蔵型NOx触媒30aには、NOxのみならず、排ガス中に含まれる硫黄成分の酸化物SOxが硫酸バリウムBaSO₄などの硫酸塩X-SO₄として吸蔵される。下記の反応式に示すように、この硫酸塩X-SO₄は、吸蔵型NOx触媒30aが還元雰囲気に晒されたときにSO₂となり、この際に硫化水素(H₂S)が生成される。



NOx触媒30aに硫酸塩が付着しているとそのNOx浄化効率が低下するので、硫酸塩の除去を企図して、一般には、NOx触媒温度を上昇させると共に混合気をリッチ化する所謂強制Sバージが周期的に実施されるが、この際に異臭を放つH₂Sが生成される。また、車両の登坂路走行時や加速運転時のようにエンジン1が高負荷域で運転される場合、エンジン1がリッチ空燃比で運転されるとともにNOx触媒温度が上昇するので、硫酸塩からSO₂が脱離して放出され、これに伴ってH₂Sが生成される(自然Sバージ)。

【0018】上記の反応式から明らかなように、H₂Sの生成量は、NOx触媒30aへの硫酸塩(S成分)の付着量が増大するほど大きくなる。NOx触媒へのS成分の付着量すなわち吸蔵量は、三元触媒の場合に比べて多く、NOx触媒を備えた排気浄化装置では多量のH₂Sが生成される傾向がある。本実施形態では、強制Sバージ中や自然Sバージ中における大気へのH₂Sの放出を抑制するべく、三元触媒30bに対してH₂S放出抑制剤としての酸化ニッケルを添加している。この酸化ニッケルは、下記の反応式に示すように、NOx触媒30aから放出されたH₂Sを硫化ニッケルに転化させるよう作用し、従って、酸化ニッケルを添加してなる三元触媒30bはH₂Sを吸蔵する機能を奏すことになる。斯く吸蔵されたH₂Sは、酸化雰囲気中で酸素と反応して臭気の少ないSO₂に転化し放出される。



50 上記の反応式から明らかなように、三元触媒30bへの

酸化ニッケルの添加量が多いほど、三元触媒30bのH₂S吸蔵能力が高まるが、一方では、三元触媒30bの三元機能が低下する傾向がある。

【0020】本実施形態では、NO_x触媒30aからH₂Sが多量に放出された場合にもH₂Sを吸蔵可能とするようなH₂S吸蔵能力を担保するべく、酸化ニッケルの添加量の下限値は、三元触媒30bの容量1リットルあたり10グラム以上、好ましくは15グラム以上の値に定められる。また、三元触媒30bの三元機能の低下を許容可能なものに留めるべく、酸化ニッケルの添加量の上限値は、35グラム以下、好ましくは25グラム以下の値に定められる。なお、酸化ニッケルに代えてニッケルを添加しても良く、この場合、ニッケルの添加量の上下限値は、酸化ニッケル添加量の上下限値に換算することにより求めることができる。更に、H₂S放出抑制剤として、Pd、Mn、Fe、Zn、Co、Cuなどを用いても良い。H₂S放出抑制剤の添加量は、添加剤の種類によってH₂S放出抑制が異なるためその好適値を異にするが、NO_x吸蔵剤添加量に対するモル比で30%ないし300%の範囲内の値が好適である。

【0021】上記のように構成された本実施形態の排気浄化装置によれば、エンジン1の冷態始動時などにおいても近接三元触媒20が速やかに活性化されて排気浄化が行われ、また、エンジン1のリーン燃焼運転時にはNO_x触媒30aによりNO_xが吸蔵される。更に、高負荷域でのエンジン運転に伴う自然Sバージ時には、NO_x触媒30aから放出されるH₂SがNiO添加の三元触媒30bによりNiSの形で吸蔵されて大気中へのH₂Sの排出が抑制される。

【0022】本実施形態の排気浄化装置は、NO_x触媒30aの所要のNO_x浄化効率を維持するべく、強制Sバージ（より一般的にはNO_x触媒からのS成分の放出を促す硫黄成分放出制御）を実施可能になっている。この強制Sバージは、排気浄化装置の制御手段の制御下で実施される。本実施形態では、エンジン1の運転制御を司る電子コントロールユニット（ECU）40が、この制御手段の機能を併有している。

【0023】ECU40は、入出力装置、記憶装置（ROM、RAM、不揮発性RAM等）、中央処理装置（CPU）、タイマカウンタ等を備え、その入力側にはスロットルセンサ11a、クランク角センサ13、高温センサ16、NO_xセンサ32等の各種センサ類が接続され、その出力側には点火プラグ4や燃料噴射弁6等が接続されている。

【0024】エンジン運転制御に関する限り、ECU40は、各種センサ類から入力した検出情報に基づいて燃料噴射モードを選択すると共に燃料噴射量や点火時期などを演算するようになっている。例えば、スロットルセンサ11aからのスロットル開度情報θ_{th}とクランク角センサ13からのクランク角情報を基づいて検出したエン

ジン回転速度情報N_eに基づいてエンジン負荷に対応する目標筒内圧（目標平均有効圧P_e）が求められ、この目標平均有効圧P_eとエンジン回転速度情報N_eとに応じて燃料噴射モードが設定される。そして、目標平均有効圧P_eとエンジン回転速度N_eから設定される目標空燃比（目標A/F）に基づいて燃料噴射量が決定される。

【0025】本実施形態では、図2に示すH₂S放出抑制制御ルーチンがECU40により実施され、この制御ルーチンで強制Sバージを行うようしている。なお、NO_xバージのための空燃比制御がECU40の制御下で実施されるが、斯かる空燃比制御は従来公知であり、その説明を省略する。図2のH₂S放出抑制制御ルーチンでは、Sバージ条件が成立しているか否かが判別される（ステップS1）。Sバージ条件は種々に設定可能であり、例えば、前回の強制Sバージが終了した時点からのリーン燃焼運転の合計実行時間が所定時間に達したときにSバージ条件の成立を判別可能である。本実施形態では、NO_x触媒30aに吸蔵されたSO_xの推定量Q_sが所定量に達したときにSバージ条件の成立を判別するようしている。

【0026】このSバージ条件判別にあたり、推定SO_x吸蔵量Q_sが例えば次式（1）から求められる。

$$Q_s = Q_{s(n-1)} + \Delta Q_f \cdot K - R_s \quad \dots (1)$$

$$K = K_1 \cdot K_2 \cdot K_3 \quad \dots (2)$$

$$R_s = \alpha \cdot R_1 \cdot R_2 \cdot dT \quad \dots (3)$$

ここで、Q_{s(n-1)}は推定SO_x吸蔵量の前回値、△Q_fは本制御ルーチンの実行周期当たりの燃料噴射積算量を示す。

【0027】Kは、上記の式（2）から演算される補正係数であり、空燃比A/F、燃料中のS含有量および触媒温度T_{cat}のそれぞれに応じた被毒度合を表す3つのS被毒係数K₁、K₂及びK₃の積で表される。R_sは、制御ルーチン実行周期当たりの放出S量を示し、上記の式（3）から求められる。式（3）中、αは単位時間当たりの放出率（設定値）であり、dTは燃料噴射制御ルーチンの実行周期を示し、R₁及びR₂は、触媒温度T_{cat}および空燃比A/Fのそれぞれに応じた放出能力係数を示す。

【0028】触媒温度T_{cat}は、高温センサ16により検出された排気温度を温度補正マップ（図示略）から読み出した補正係数および排気流速を用いて補正することにより求められる。温度補正マップは予め実験等により設定されるもので、この温度補正マップにおいて、定常時の触媒温度T_{cat}と排気温度との補正是、目標平均有効圧P_eとエンジン回転速度情報N_eとの関数で与えられる。

【0029】Sバージ条件の成立がステップS1で判別された場合、Sバージモードが設定されると共にSバージモード設定時点からの経過時間を計測するタイマがリ

セットされてから起動される（ステップS2）。そして、H₂S放出速度すなわち時間に対するH₂S濃度の増加度合が所定値を上回っているか否かが判別される（ステップS3）。

【0030】H₂S放出速度は、センサにより検出される実際のH₂S放出速度情報から検出しても良いが、本実施形態では、エンジン回転数N_e、目標平均有効圧P_e、1吸気行程あたりの吸入空気量A/N、車速、触媒温度T_{cat}、排気温度、エンジン冷却水温などの関数で表されるエンジン運転状態に基づいてH₂S放出速度を推定するようしている。

【0031】すなわち、各種エンジン運転状態におけるH₂S放出速度を求める実験が行われ、実験結果に基づいてマップが予め作成され、ECU40の記憶装置に格納される。そして、ECU40の制御下でのエンジン運転中、このマップから、エンジン運転状態に応じたH₂S放出速度を求めることになる。図示を省略するが、マップにおいて、一般には、エンジン回転数N_eやエンジン負荷（目標平均有効圧P_e、吸入空気量A/N）の増大ならびに触媒温度T_{cat}や排気温度の上昇につれてH₂S放出速度が増大するように、エンジン運転状態とH₂S放出速度とが関連づけられる。

【0032】H₂S放出速度の判定のための所定値は、排気管14の出口付近にいる人々にH₂Sの臭気を感じさせるようなH₂S濃度の下限値に対応する値（以下、限界値という）に設定される。この限界値は、特に車速に応じて変化する。すなわち、車両走行時にはたとえ排気管14からH₂Sが放出されたとしてもH₂Sは大気中へ速やかに拡散され、臭気を感じる限界値は比較的高くなる。一方、車両走行停止時にはH₂Sは拡散し難く、限界値は小さなものになる。従って、H₂S放出速度の所定値は車速に応じて設定することが好ましく、本実施形態では、車速の関数として表される限界値を予めマップ化しておき、車速に応じて定まる限界値をマップ（図示略）から読み出すようしている。但し、H₂S放出速度の所定値を可変設定することは必須ではなく、固定値を用いても良い。

【0033】一般に、Sバージモード設定直後にあっては、H₂S放出速度は所定値を上回らず、ステップS3での判別結果は否定（No）になる。この様にH₂S放出速度が小さいという要件が満足された場合、Sバージ運転が行われる（ステップS4）。Sバージ運転では、吸蔵型NO_x触媒30aを還元雰囲気に晒すべく、目標A/Fを所定のリッチ空燃比（例えば1.2）に設定してリッチ空燃比運転を実施し、排気空燃比をリッチ空燃比とする。また、点火時期を遅角させて排気ガス温度を上昇させ、これによりNO_x触媒30aを昇温させる。この様なリッチ空燃比でのエンジン運転により、燃料の不完全燃焼が起こり、硫黄酸化物SO_xの除去に必要な一酸化炭素や炭化水素が多量に発生してNO_x触媒30a

に供給され、点火時期の遅角制御による排気温度上昇に伴うNO_x触媒温度の上昇と相まって、Sバージを促進する。

【0034】本実施形態では、上記のように設定される目標A/Fに基づいてECU40により燃料噴射量が決定され、この燃料噴射量に対応する駆動信号に従って燃料噴射弁6が開閉駆動され、また、必要に応じて吸入空気量が調整される。従って、ECU40、燃料噴射弁6、吸入空気量調整に係る制御バルブ要素（図示略）ならびにECU40に内蔵のタイマにより、排気空燃比を所定期間にわたり理論空燃比またはリッチ空燃比に維持する空燃比固定手段が構成されることになる。

【0035】さて、Sバージの進行によってSO_xの放出が進むと、リッチ空燃比の下でH₂Sが生成されるが、NO_x触媒30aの下流に設けた三元触媒30bに添加されている酸化ニッケルにより、H₂Sが硫化ニッケルに転化される。この様に、H₂Sが三元触媒30bに吸蔵されるので、大気中へ放出される排ガス中のH₂S濃度が低減される。

【0036】Sバージ運転に係るステップS4に続いて、ステップS2で起動されたタイマによる経時時間を参照して、Sバージモードが所定時間（所定期間）にわたって維持されたか否かが判定される（ステップS5）。Sバージ維持時間が所定時間に満たなければ、NO_x触媒30bからのS成分除去が充分に行われていないと判断してステップS3に戻る。尚、Sバージ運転の終了の判定は、推定SO_x吸蔵量Q_sが所定量以下となることを条件として判定してもよい。

【0037】上記のようにNO_x触媒30aでのS成分の還元に伴って発生するH₂Sは三元触媒30bに吸蔵されるが、NO_x触媒30aに吸蔵されていたS成分量が多いなどの理由で、Sバージ運転中にH₂S放出速度が一時的に高まることがある。この場合、H₂S放出速度が所定速度を上回ったことがステップS3で判別されると、H₂S放出速度を低減するべく、Sバージ運転からH₂S放出抑制運転への切換えが行われる（ステップS6）。

【0038】このH₂S放出抑制運転では、ECU40により、目標A/Fが理論空燃比を境として変調される。すなわち、図3に示すように、目標A/Fは、所定期間T_{cycle}毎に、リッチ側の第1目標A/Fまたはリーン側の第2目標A/Fに交互に設定される。ここで、第1及び第2目標A/Fは、H₂S放出抑制運転における目標A/Fの平均値をSバージを促進可能な値（例えばスライトリッチである約1.4、3或いはリッチ側の約1.2）とするような値にそれぞれ設定される。そして、この様にして設定される目標A/Fに基づいてECU40により燃料噴射量が決定され、この燃料噴射量データに従って燃料噴射弁6が開閉駆動され、また、必要に応じて吸入空気量が調整される。従って、ECU40

は、燃料噴射弁6や吸入空気量調整に係る制御バルブ要素(図示略)と共に、ほぼ理論空燃比を基準にして排気空燃比をリッチ側とリーン側とに交互に変動させる空燃比変動手段を構成している。

【0039】上記のH₂S放出抑制運転は、三元触媒30bに添加された酸化ニッケルのH₂S吸蔵・放出機能を最大限に活用することを企図したものである。すなわち、リッチ空燃比運転(還元雰囲気)での酸化ニッケルによるH₂S吸蔵作用(H₂S + NiO → NiS + O₂)が飽和する前にリッチ空燃比運転からリーン空燃比運転(酸化雰囲気)へ切換え、三元触媒30bに硫化ニッケルの形で吸蔵されたH₂Sを臭気の少ないSO₂に転化するものである(NiS + 3/2 * O₂ → NiO + SO₂)。

【0040】なお、リッチ空燃比とリーン空燃比の間で空燃比を所定周期で切り替える上記のA/F変調に代えて、所定のリッチ化時間にわたるリッチ空燃比運転と所定のリーン化時間にわたるリーン空燃比運転とを交互に実施するようにしても良い。この場合、三元触媒30bに添加された酸化ニッケルによるS成分捕捉作用が飽和するに至る飽和時間、および、硫化ニッケルの形で捕捉したS成分をSO₂として放出するのに要する放出時間が、エンジン運転状態などに応じて変化することを勘案して、リッチ化時間およびリーン化時間を設定することが好ましい。すなわち、好ましくは、リッチ化時間およびリーン化時間のそれぞれを、エンジン運転状態などに応じて決まる飽和時間および放出時間に等しい値に設定する。但し、リッチ化時間およびリーン化時間を固定値に設定してもH₂S抑制効果を得ることができる。

【0041】図4は、点火時期の遅角制御によるNOx触媒30aの温度上昇に伴う三元触媒30b下流の排ガス中のH₂S濃度の変化を、空燃比を一定値14.3に維持した場合および平均空燃比が値14.3となるようなA/F変調を行った場合について示す。図4からわかるように、一定の空燃比での機関運転の場合に比べて、機関運転中に空燃比をリッチ側とリーン側との間で周期的に切り替えるA/F変調を行うことにより、空燃比が同等であるにもかかわらず、H₂Sの放出が抑制されることが分かる。

【0042】ステップS6でのH₂S放出抑制運転が実施されると、排ガス中のH₂S濃度が減少し、従って、H₂S放出速度も減少する。このH₂S放出速度の低下により、H₂S放出に伴う臭気の度合が低減する。ステップS6に続くステップS5ではSバージモード設定時点から所定時間が経過したか否かが判別され、この判別結果が否定であれば、ステップS3に戻る。

【0043】この様にして、Sバージモード設定時点から所定時間が経過するまでは、H₂S放出速度が所定値を上回るか否かに応じて、Sバージ運転またはH₂S放出抑制運転が選択的に実施される。そして、Sバージモ

ード設定時点から所定時間が経過したことがステップS5で判別されると、NOx触媒30aに吸蔵されていたS成分の放出、すなわちNOx触媒30aの浄化能力の再生が充分に行われたと判断され、Sバージモードが解除され(ステップS7)、強制Sバージ制御が終了する。

【0044】ステップS1においてSバージ条件の不成立が判別されると、H₂S放出速度が所定値を上回っているか否かが判別される(ステップS8)。このステップS8での判定は上記ステップS3での判定と同様に行われる所以、その説明を省略する。そして、H₂S放出速度が所定値を上回っていることがステップS8で判別されると、H₂S放出抑制運転が行われる(ステップS9)。ステップS9でのH₂S放出抑制運転は上記ステップS6のものと同様であり、その説明を省略する。以上のようにして、Sバージ運転中でない場合にも例えば自然SバージによってH₂S放出速度が増大するとH₂S放出抑制運転が実施されて、H₂Sの放出に伴う臭気の発生が未然に防止される。

【0045】本発明は、上記実施形態のものに限定されず、種々に変形可能である。例えば、上記実施形態では、NOx触媒30aからの硫黄成分の放出を促す硫黄成分放出制御(強制Sバージ)を実施するようにしたが、本発明の排気浄化装置は自然SバージによるH₂Sの放出に際しても、例えば上記実施形態のA/F変調(図2のステップS9)を実施することによりH₂S放出速度を抑制可能であるので、本発明で強制Sバージ(空燃比固定)を実施することは必須ではない。

【0046】また、実施形態では、排気浄化装置の触媒システムを、近接三元触媒とその下流に配された排気浄化触媒装置とで構成すると共に、排気浄化触媒装置のNOx触媒の下流に三元触媒をH₂S放出抑制触媒として設けたが、本発明において、この様な構成は必須でなく、排ガス中のNOxを吸蔵、排出可能なNOx吸蔵触媒装置を備えたものであれば良い。そして、NOx吸蔵触媒装置の下流にH₂S放出抑制触媒を具備しない排気浄化装置においても、NOx吸蔵触媒装置からのH₂S放出速度に応じて例えば上記のA/F変調を実施することにより、放出H₂Sによる臭気の発生を抑制しつつ、S被毒されたNOx吸蔵触媒装置の浄化能力を再生可能である。

【0047】本発明において硫黄成分放出制御(強制Sバージ)を行う場合、強制Sバージのための制御手段は、実施形態のように、内燃機関に供給される混合気の空燃比をリッチ空燃比に制御する空燃比制御手段(空燃比固定手段)とNOx吸蔵触媒装置を昇温させる昇温制御手段とから構成可能であるが、これに限定されず、空燃比制御手段または昇温制御手段の一方からなる強制Sバージ制御手段を構成できる。

【0048】昇温制御手段は、実施形態のように、点火

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時期を遅角させる点火時期制御手段からなる構成としても良いが、これに限定されない。例えば、筒内噴射式の希薄燃焼内燃機関の場合には主たる燃料噴射に加えて膨張行程で追加燃料噴射を行わせる燃料噴射制御手段により昇温制御手段を構成可能である。また、昇温制御手段は、NO_x吸蔵触媒装置の温度が、その活性温度よりも高く且つNO_x吸蔵触媒装置に吸蔵された硫黄成分の脱離に適した温度またはそれよりも低い設定温度以上になったときに、NO_x吸蔵触媒装置をアシスト的にさらに昇温するものでも良い。

【0049】強制Sバージ制御手段を備えた排気浄化装置によれば、NO_x吸蔵触媒装置による硫黄成分(S成分)の吸蔵量が増大したときに硫黄成分放出制御(Sバージ)が行われ、この結果、NO_x吸蔵触媒装置がリッチ空燃比およびまたは高温の雰囲気に晒され、NO_x吸蔵触媒装置からのS成分の放出が促され、所要のNO_x浄化効率が維持される。

【0050】また、強制Sバージ制御手段は、触媒再生情報または硫黄成分による被毒情報に応動するものでも良く、例えば、触媒再生情報に基づいて所定期間内における触媒再生頻度(硫黄成分の脱離が行われる頻度)が所定頻度よりも少ないことが判別されたとき、或いは、被毒情報から推定される被毒量が所定値よりも大きいときに、硫黄成分放出制御を行うもので良い。被毒情報は、希薄燃焼内燃機関の燃料消費量や運転時間(車両走行距離)から、または排ガス中のNO_x濃度を検出するNO_xセンサの出力から求めることができる。

【0051】

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* 【発明の効果】本発明の排気浄化装置は、機関運転状態に基づいて推定されるNO_x吸蔵触媒装置からの硫化水素放出速度に基づいて空燃比変動手段を作動させ、これによりほぼ理論空燃比を基準にして排気空燃比をリッチ側とリーン側とに変動させてるので、硫化水素(H₂S)を含む排ガスの大気中への放出による臭気の発生を抑制しつつ、S被毒されたNO_x触媒装置の浄化能力を再生することができる。

【図面の簡単な説明】

10 【図1】本発明の一実施形態による排気浄化装置を装備した内燃機関の概略図である。

【図2】図1に示した電子制御ユニットにより実施される強制Sバージ制御ルーチンのフローチャートである。

【図3】図3の制御ルーチンで実施されるSバージ抑制運転のためのA/F変調における目標A/Fの時間的変化を示す図である。

【図4】触媒温度上昇に伴う排ガス中のH₂S濃度の時間変化を、一定空燃比での機関運転およびA/F変調を伴う機関運転の双方について示す図である。

20 【符号の説明】

1 エンジン(希薄燃焼内燃機関)

6 燃料噴射弁(空燃比変動手段)

14 排気管(排気通路)

30 排気浄化触媒装置

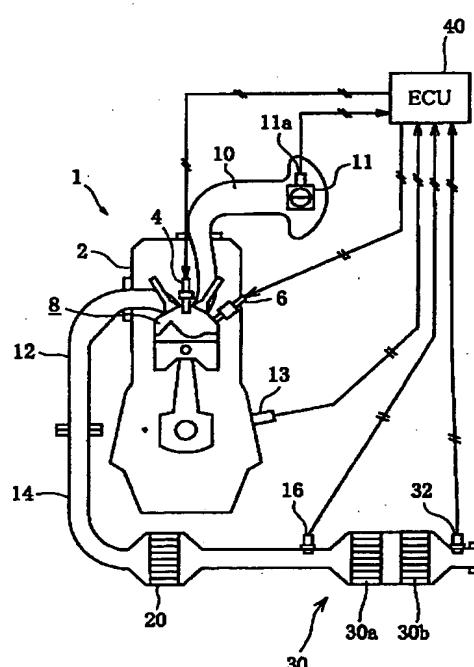
30a NO_x触媒(NO_x吸蔵触媒装置)

30b 三元触媒(H₂S放出抑制触媒装置)

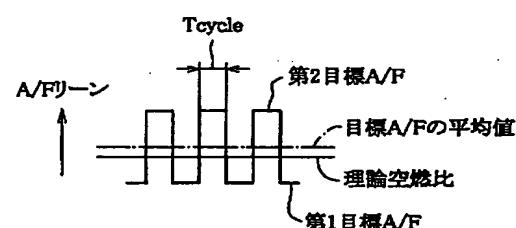
40 電子制御ユニット(空燃比変動手段、制御手段)

*

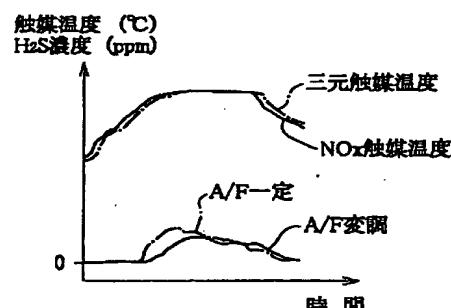
【図1】



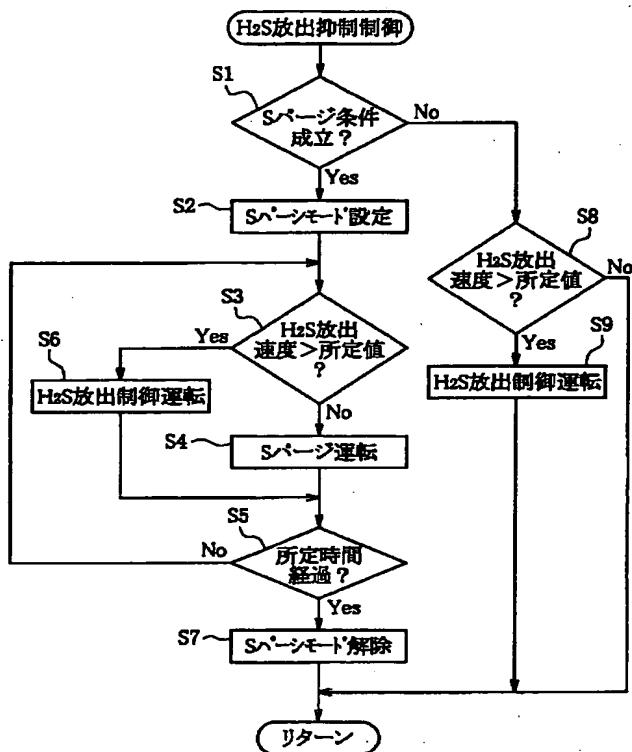
【図3】



【図4】



[図2]



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